June 30, 1970 E. J. LEVY 3,518,059

METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

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Fig. 1.

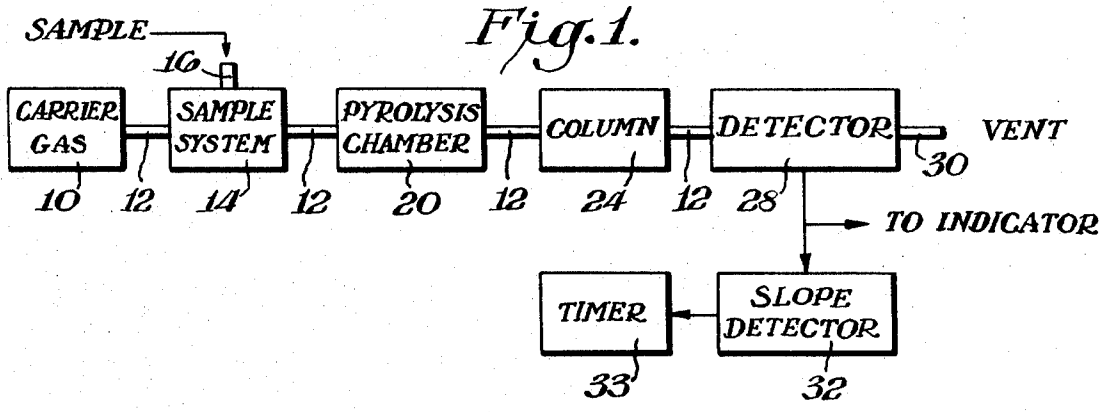


Fig. 3.

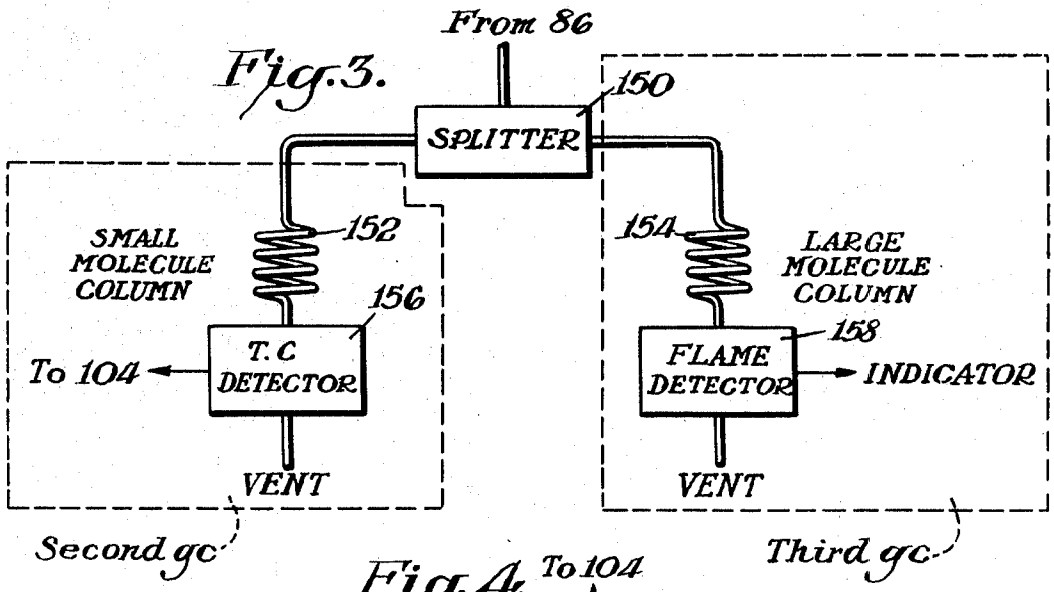
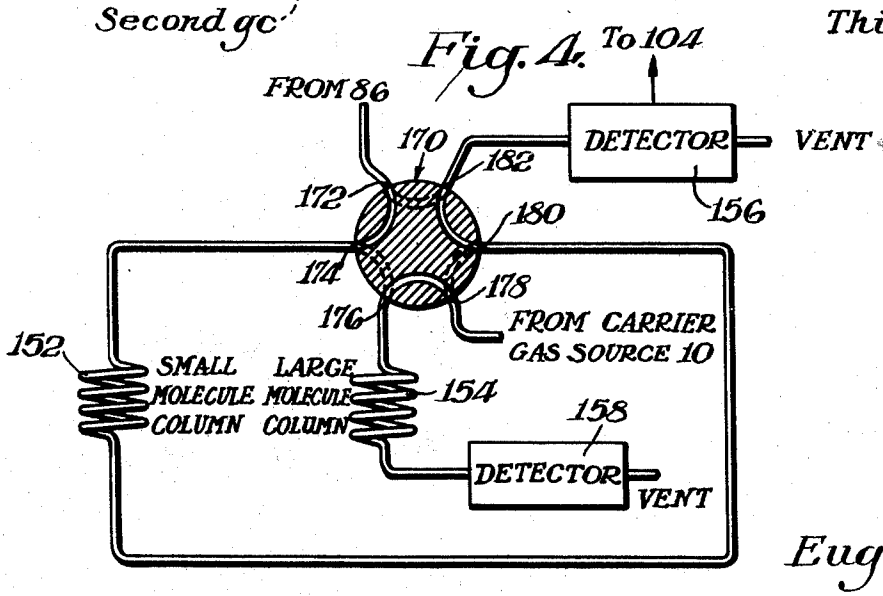


Fig. 4.



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METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

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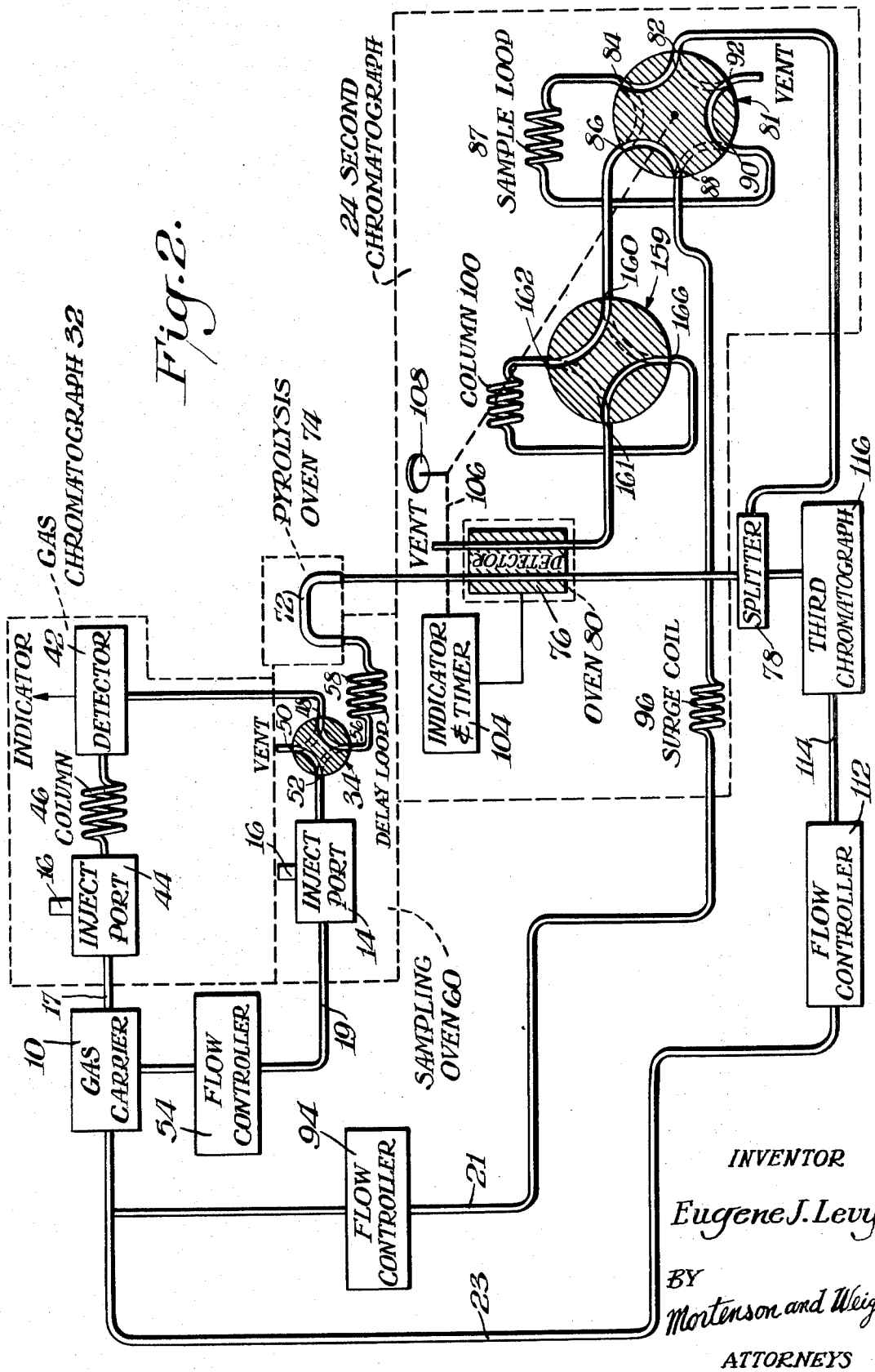
Fig. 2.



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METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

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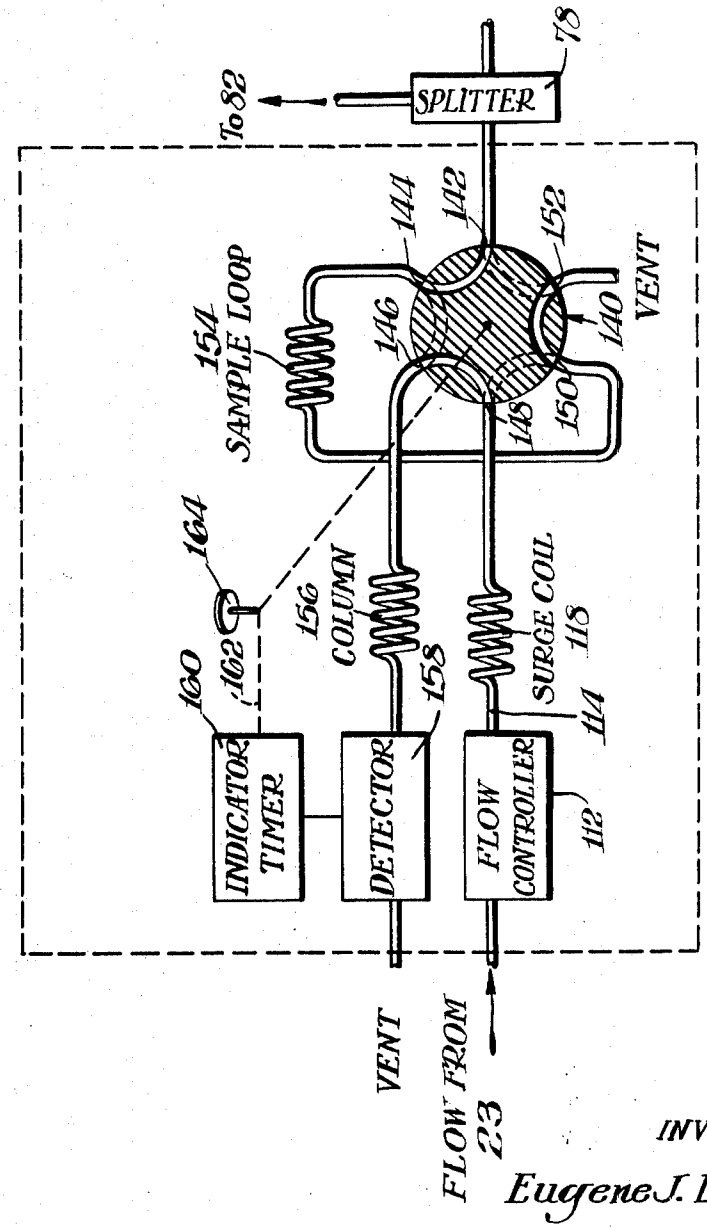
Fig. 2a.



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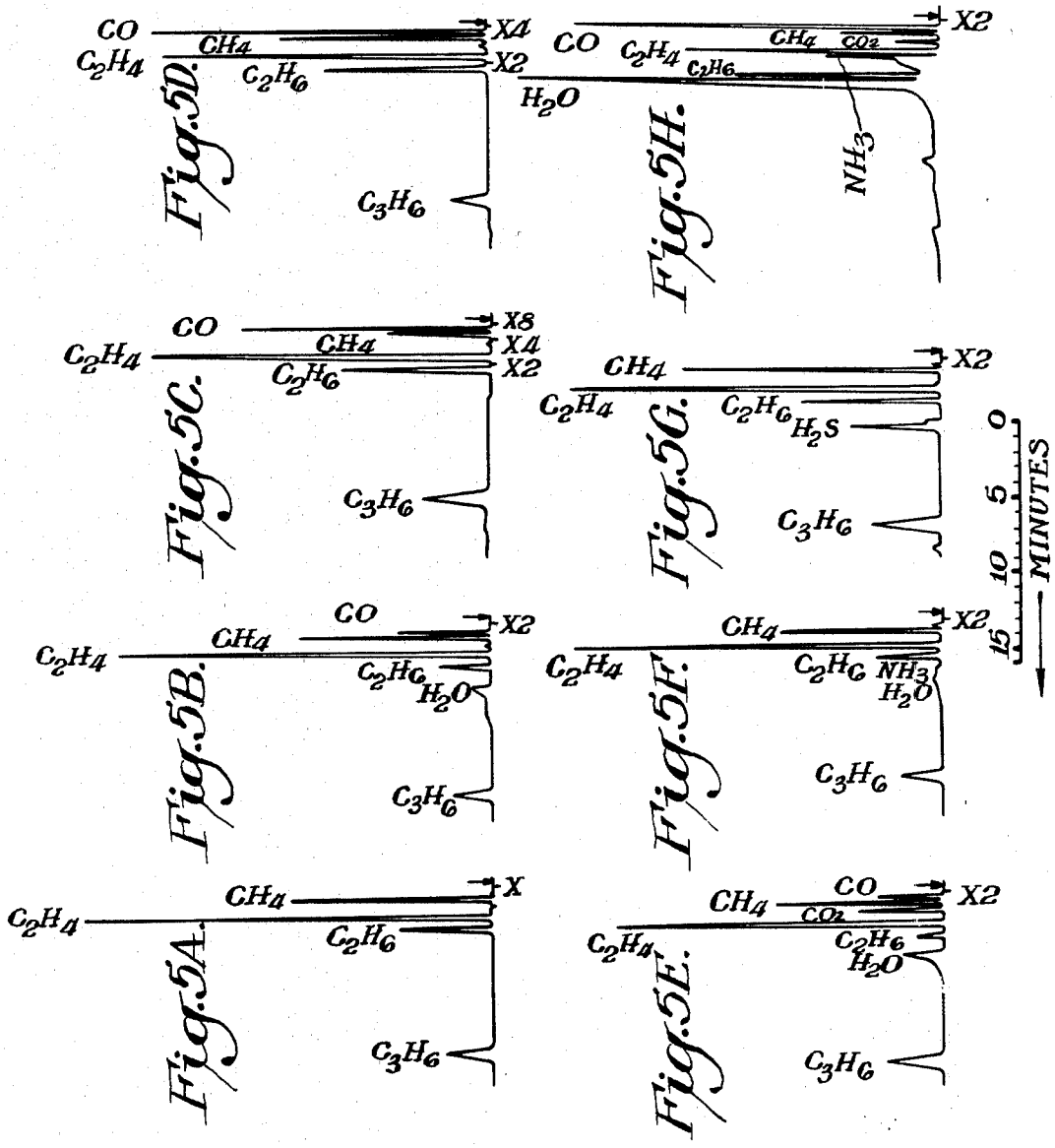
METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

Filed May 31, 1967 5 Sheets-Sheet 4



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METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

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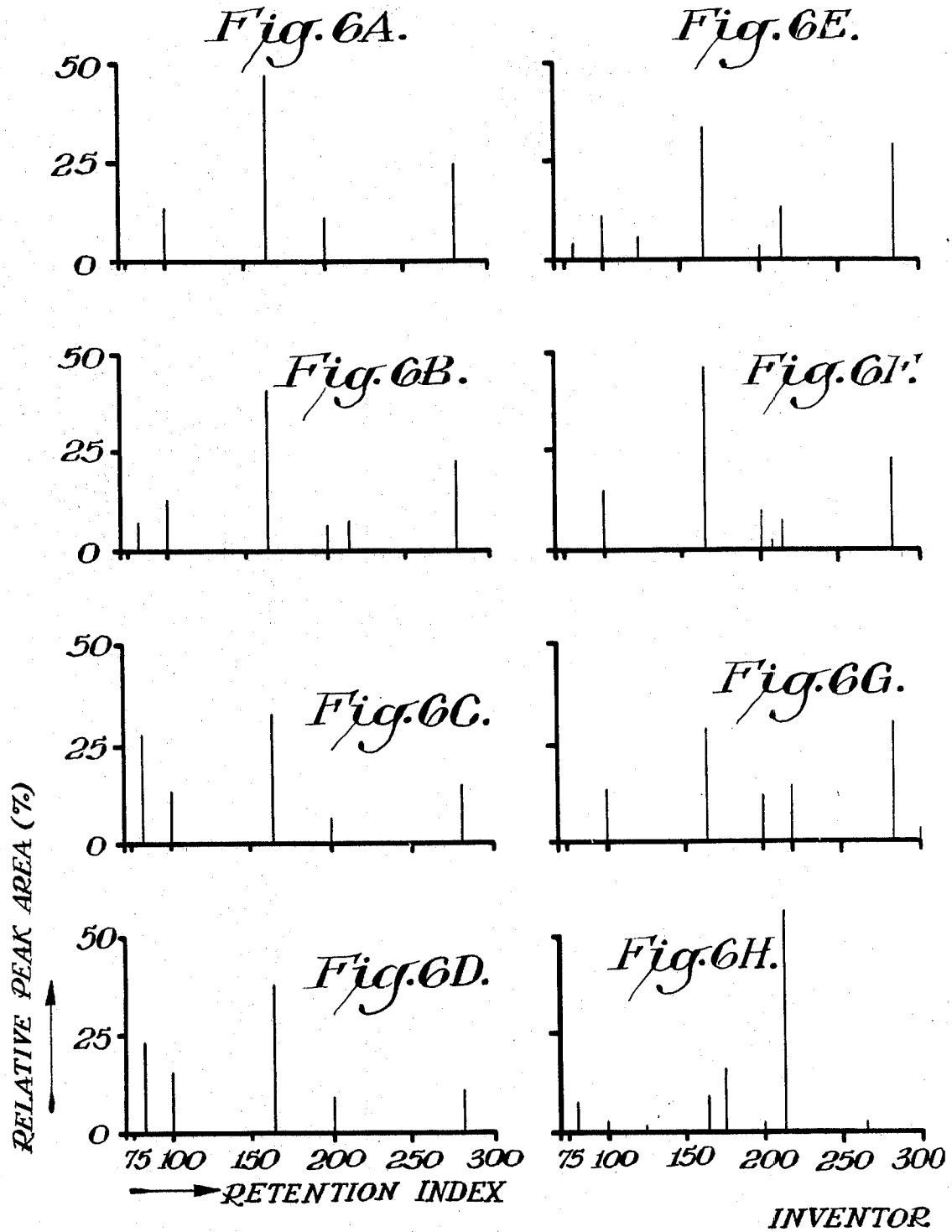

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3,518,059

METHOD AND APPARATUS FOR DETERMINING CHEMICAL STRUCTURE

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Filed May 31, 1967, Ser. No. 646,443
Int. Cl. G01n 31/08
U.S. Cl. 23—232 5 Claims

ABSTRACT OF THE DISCLOSURE

A method of and apparatus for pyrolyzing chemical compounds and using their volatile and non-volatile thermolytic dissociation products to obtain partial cracking patterns which are directly relatable to the molecular structure and the functional groups present in the original chemical compounds. The compounds are cracked in a pyrolyzer and the resulting product stream is divided into two portions by a splitter which simultaneously feeds one portion to a first chromatograph to obtain a cracking pattern for the volatile products in the product stream and the second portion to a second chromatograph to obtain a cracking pattern for the less volatile products in the product stream.

This invention relates to a method for identifying the chemical nature of compounds and, more particularly, to a method and apparatus for pyrolyzing compounds and observing their volatile and non-volatile components as an aid in identifying the compounds.

In recent years, gas chromatography has proven to be an extremely useful and effective separating technique by which sample mixtures may be separated into their components. The relative quantity of each component may be readily determined with the aid of any one of many gas detectors. While quite satisfactory for quantitative analyses, difficulties are encountered in identifying the separated components. To identify such components, resort usually is had to whatever auxiliary analytical tools are available. Optical or mass spectrometers have been used for such identifications, but usually these are quite costly. Infrared and ultraviolet spectrometers can also be used, but in many cases these give limited information. Additionally, the infrared spectroscopic method has the disadvantage of requiring relatively large quantities of the sample for a definite identification.

It is, therefore, an object of this invention to facilitate the identification of substances using pyrolysis techniques.

Keulemans and Perry described an identification system using a pyrolysis tube and a gas chromatograph in a paper entitled "Identification of Hydrocarbons by Thermal Cracking" presented at the Fourth International Gas Chromatography Symposium, Hamburg, Germany, 1962. A reprint of the Kuelemans et al. paper was published in 1962 in London by Butterworth. As proposed by Keulemans et al., a sample is passed by menas of a carrier gas through a continuous flow system including a pyrolysis chamber and a gas chromatograph located dowstream of the pyrolysis tube. The most volatile, low molecular weight products are discarded and higher molecular weight products, which are gaseous under the conditions used, are separated by the gas chromatograph and individually detected and recorded as a chromatogram. By determining the relative quantities of the said larger decomposition products, distinctive and reproducible patterns, called cracking patterns, are obtained and the observed cracking pattern is closely related to the carbon skeleton of the parent organic molecule.

An improved method and system for obtaining these

cracking patterns is described and claimed in the U.S. Pat. No. 3,425,807, issued Feb. 4, 1969 entitled "Pyrolysis Systems" by Eugene J. Levy. To obtain better reproducibility of the cracking patterns, the pyrolysis pressure, temperature and residence time of the sample in the pyrolysis unit must be maintained within certain carefully controlled limits as pointed out by Levy. To overcome many of these deficiences and to facilitate the handling of relatively small samples, Levy describes an apparatus and a method for identifying a sample component by introducing the sample mixture into a first flow system, separating the components of the sample mixture in the first flow system, introducing one of the separated components into a second flow system, pyrolyzing such separated component in a second flow system and introducing the pyrolysis products in a third flow system in order to separate and obtain a cracking pattern which is indicative of the sample component, the most volatile, low molecular weight products again being completely ignored as in the Keulemans et al. teaching.

In the Levy system, valves interconnect the several flow systems to permit a discrete portion of the first flow system to be sampled and passed on for pyrolysis. In like manner, the pyrolysis products are taken from the second flow system and introduced into the third flow system for separation and detection. Information as to the relative quantities of pyrolysis products affords a means of identifying the parent molecule.

The Levy and other prior art systems make use only of the large (higher molecular weight) molecules in the pyrolyzate to obtain the thermal cracking pattern which is related to the carbon skeleton of the parent molecule of the individual sample being analyzed.

It is an object of this invention to utilize the small (lower molecular weight) molecules resulting from the thermal decomposition of samples as an additional means of identifying the parent compounds, especially in relation to the determination and identity of functional groups present in the original compounds.

Another object of this invention is to provide an improved method of applying pyrolysis to the identification of compounds present in a sample of material.

Another object of this invention is to provide an improved system for identifying substances by pyrolysis techniques.

In accordance with the illustrated method of this invention, a sample of a mixture of components is analyzed. The preferred method includes introducing the sample into a first chromatographic column, separating the sample into certain of its components in the first column, eluting one of the said components and pyrolyzing it to produce pyrolysis products including heavy (molecular weight) constituents as well as light (molecular weight) constituents, passing the pyrolysis products to a second chromatographic system, separating the light constituents of the pyrolysis products in the second column, detecting each of these constituents on elution from the second column, and measuring the retention times in the second column of said constituents, thereby relating the presence and relative quantities of these light constituents to the functional groups and structures present in the originally separated components.

One embodiment of the apparatus of this invention includes a sample injection means, a pyrolysis chamber, a chromatograph column capable of separating light pyrolyzate products, a sample loop, and first and second detectors. Also included is a valve means for alternatively passing the sample from the injection means through the pyrolysis chamber, sample loop, and first detector when the valve is in a first postion and from the sample loop where it is stored through the column and second detector when the valve is in a second position, whereby the pyroly-

sis products are separated by the column and detected by the second detector. A timer is employed to measure the the time required for the several pyrolysis products to pass through the separating column. This time is related to the chemical structure of the low molecular weight pyrolysis products and these determine the identity of the parent molecule.

The novel features that are considered characteristic of this invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and method of operation, as well as additional objects and advantages thereof will best be understood from the following description when read in connection with the accompanying drawings, in which:

FIG. 1 is a block-flow schematic diagram illustrating a system capable of performing the method of this invention;

FIG. 2 is a detailed part schematic and part block diagram of a system suitable for performing the method of this invention by isolating the flow streams of the separating and pyrolyzing system.

FIG. 2A is a block-flow schematic diagram of the detail of the third chromatograph shown in FIG. 2;

FIG. 3 is a block-flow schematic diagram of an alternative embodiment of this invention that may be employed in connection with the system illustrated in FIG. 2;

FIG. 4 is a block-flow schematic diagram illustrating still another alternative embodiment that may be employed in connection with the system illustrated in FIG. 2 for performing the method of this invention;

FGIS. 5A–H are a series of pyrograms in which the detector output signal amplitude as the ordinant is plotted against retention time as the abscissa to show the retention times and quantities of small molecules present in the products produced by pyrolyzing several different parent molecules; and

FIGS. 6A–H are a series of bar graph representations of the total area of each small molecule of the pyrolysis products plotted against relative retention time for each of the several different parent molecules.

According to the preferred method of this invention, a chemical sample to be identified is introduced successively into three separate flow systems or streams. The first and third flow systems are gas chromatographs, and the second, or intermediate, flow system is a pyrolysis chamber. Although preferred, the first gas chromatograph may be eliminated from the system to provide a more simple system of the type illustrated in FIG. 1. As used herein "flow stream" is intended to denote a complete integrated flow system which includes a suitable conduit for providing a confined path for gases and vapors between elements of the system.

In FIG. 1 there is seen a source of carrier gas **10** which may be any of the suitable carrier gases employed in gas chromatography and preferably should be inert. By the term "inert" is meant a gas that does not pyrolyze and is nonreactive with the sample undergoing the analysis at the respective temperatures that exist throughout the system. A suitable gas that serves this purpose is helium. The carrier gas source **10** is connected by means of a conduit **12** to a sampling system **14** of suitable design and thence to the remaining elements of the system. The sampling system **14** may be no more than a conventional injection port permitting the sample to be introduced, as by a suitable sampling syringe, through a septum **16**. The output of the sampling system **14** is connected through successive conduits **12** to a pyrolysis chamber **20**, a gas chromatograph separating column **24**, and a detector **28** to a vent to atmosphere **30**.

The pyrolysis chamber **20** may be a suitable non-reactive tube of appropriate diameter and length, as will be described in more detail in connection with FIG. 2, heated to obtain thermal decomposition of the sample components passed therethrough. The gas chromatograph column **24** may contain any suitable column material adapted to separate molecules of lighter molecular weight constituents, typically organic through C_4 and small polar molecules such a water, H_2S, NH_3, SO_2, etc. A suitable column for this purpose, as will be described with more detail in connection with FIG. 2, may be one packed with a bed of an insoluble cross-linked, finely divided microporous, organic polymer such as a copolymer of divinyl benzene and ethyl vinyl benzene. A column packing of this type, sold under the trade name "Porapak" is available from Waters Associates, Inc., Framingham, Mass. Other suitable packing may be used such as a silicon oil column on a "Teflon" support.

The detector **28** preferably is a non-destructive type detector such as the well-known thermal conductivity detector in which changes in the resistance of a resistance element occur in accordance with the thermal conductivity of a mixture of carrier gas and sample components. The detector's resistance element is placed in a bridge circuit to provide an electrical output signal. The electrical output signal from the detector **28** is amplified and may be applied to a suitable indicator such as an industrial chart-type recorder. The retention time of each separated component is measured. These retention times depend upon the chemical structure of the light constituents, i.e., small molecules or low boilers, eluted from the column. Knowledge as to the identity of these low boilers aids in the determination of the identity of the original molecule introduced at the septum **16**.

The retention time may be obtained either manually from the chart record or automatically by connecting the detector output signal to a slope detector **32** and timer **33**. The slope detector **32** is a device for electronically differentiating an electrical signal to determine the rate of change of its amplitude. When the electrical signal is represented graphically, as by a recorder, the rate of change may be seen as the slope of a particular curve or wave form. One such electronic differentiating device may be constructed by connecting a capacitor and resistor in series. Depending upon the input wave form, the output from the differentiating circuit will be an electrical signal which is either zero, positive, or negative going. The magnitude of this electrical signal depends upon the rate of the change. A pip or peak in the detector output wave form, is produced by the detector's denoting the presence of a particular eluted component. This amplitude varying signal from the slope detector **32** may be passed through a suitable threshold circuit such as a Schmidt trigger, which in turn actuates the timer **33**. The timer **33**, initially manually actuated when the sample is introduced into the system, measures the elapsed time, from the time of the sample introduction until each of the sample components are detected by the detector. Another type of slope detector may utilize a voltage-to-frequency converter in which the rate of frequency variations are a measure of the slope.

As a result of the remarkable and varied capacity of carbon for combining with itself and other elements, many different types of organic compounds are possible. Many of these types of classes are characterized by particular groups of elements known as functional groups. The method of this invention is based on the discovery that if a molecule containing a functional group is pyrolyzed under the proper conditions, as taught by the said Levy patent, the molecule will dissociate into smaller molecules which include certain low boiling or light (molecular weight) constituents directly relatable to the functional groups. These so called "proper conditions" are those which minimize secondary recombination reactions during pyrolysis, i.e., pyrolysis is not complete.

A few of the principal classes of organic compounds and their principal low molecular weight dissociation products are shown in the following Table I:

TABLE I

Pattern	Type	Compound	Principal products
A	Hydrocarbon	$CH_3(CH_2)_6CH_3$	CH_4; C_2H_4; C_2H_6; C_3H_6
B	Alcohol	$CH_3(CH_2)_6CH_2OH$	CO; CH_4; C_2H_4; C_2H_6; H_2O; C_3H_6
C	Aldehyde	$CH_3(CH_2)_6CHO$	CO; CH_4; C_2H_4; C_2H_6; C_3H_6
D	Ketone	$CH_3CH_2\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3$	CO; CH_4; C_2H_4; C_2H_6; C_3H_6
E	Ester	$CH_3(\overset{O}{\overset{\|}{C}}-O(CH_2)_5CH_3$	CO; CH_4; CO_2; C_2H_4; C_2H_6; H_2O; C_3H_6
F	Amine	$CH_3(CH_2)_6CH_2NH_2$	CH_4; C_2H_4; C_2H_6; NH_3; C_3H_6
G	Mercaptan	$CH_3(CH_2)_6CH_2SH$	CH_4; C_2H_4; C_2H_6; H_2S; C_3H_6
H	Ethanol amine	$NH_2CH_2CH_2OH$	CO; CH_4; CO_2; C_2H_4; C_2H_6; H_2O; NH_3

There may be seen by reference to FIGS. 5A–H typical chromatograms of low molecular weight pyrolysis, hereinafter referred to as pyrograms, illustrating retention times of many of the possible small molecules resulting from the thermal dissociation of larger molecules listed in Table I. The pattern letters A through H correspond to compounds A to H in Table I and in each pyrogram each peak is identified as to the compound to which it corresponds. The identity of each peak is established from a knowledge of typical retention times of the several compounds.

It may be noted from FIGS. 5A–H that the pyrogram resulting from the pyrolysis of each different substance A to H is a unique (no two are the same) pyrogram which is a fingerprint or indicator denoting the existence of a particular compound in the sample under analysis. The uniqueness of these pyrograms is characterized not only by the presence or absence of particular decomposition products as noted in Table I, but several peaks of the pyrograms of the particular decomposition products for that compound. For example, an aldehyde,

$$CH_3(CH_2)_6CHO$$

and having the indicated formula, includes the principal reactions CO; CH_4; C_2H_4; C_2H_6; C_3H_6. Again, the decomposition of a mercaptan, as exemplified by the compound $CH_3(CH_2)_8CH_2SH$, produces the principal reaction products CH_4; C_2H_4; C_2H_6; H_2S; C_3H_6. Even though the aldehyde C and ketone give the same products, the amounts of each differ very substantially as can be seen, to give distinctive patterns.

To illustrate the uniqueness of this identification technique, the areas under each of the pyrograms A through H in FIG. 5 were computed and converted to a percentage of the total peak areas in each pyrogram. These percentages were then plotted in bar graph form as the ordinant against relative retention times, as determined by the well-known Kovat's formula, for the abscissa. As may be seen in FIGS. 6A–H, each compound is easily distinguished from the other ones. This means that the identification of a particular functional group is possible if the pyrogram pattern of its small molecule dissociation products is known.

For example, if a particular analysis produced a pyrogram which when converted to the bar graph form resulted in an identification pattern similar to pattern D it is immediately known that the compound is ethyl pentyl ketone.

Experimental pyrograms were obtained from many different compounds. Each of the compounds listed, including the various alcohols, aldehydes, ketones, etc. were first initially pyrolyzed and their thermal dissociation products passed through the column **24** (FIG. 1) to be separated in time. As the dissociation products were eluted for each compound, they were detected by the detector **28** and recorded. Their relative peak areas and retention times (Kovat's index) were then computed and the results of the computations set forth in Table II below:

TABLE II.—COMPOSITION OF SMALL MOLECULES

Type (compound)	Retention index								Pyr. temp. °C.
	CO 80	CH_4 100	CO_2 123	C_2H_4 165	C_2H_6 200	NH_3 207	H_2O 214	H_2S 218	C_3H_6 283	
Hydrocarbon (A):										
$CH_3(CH_2)_5CH_3$		14		49	11				26	654.5
$CH_3(CH_2)_6CH_3$		15		48	12				25	655.0
$CH_3CH_2CH(CH_3)(CH_2)_2CH_3$		22		26	10				42	655.0
Alcohol (B):										
$CH_3(CH_2)_5CH_2OH$	5	14		46	7		8		20	657.0
$CH_3(CH_2)_6CH_2OH$	7	14		41	7		8		23	656.0
Aldehyde (C):										
$CH_3(CH_2)_5CHO$	25	14		37	8				17	657.0
$CH_3(CH_2)_6CHO$	28	14		34	8				15	657.0
Ketone (D):										
$CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}(CH_2)_5CH_3$	18	17		39	5				21	657.0
$CH_3CH_2\overset{O}{\overset{\|}{C}}(CH_2)_6CH_3$	20	12		41	11				16	656.5
$CH_3(CH_2)_2\overset{O}{\overset{\|}{C}}-(CH_2)_3CH_3$	17	14		34	8				27	656.5
$CH_3CH_2\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3$	23	16		39	10				12	656.0
Ester (E):										
$CH_3\overset{O}{\overset{\|}{C}}-O-(CH_2)_6CH_3$	4	11	6	33	3		13		29	656.5
$CH_3\overset{O}{\overset{\|}{C}}-O-(CH_2)_7CH_3$	5	10	6	35	4		15		25	656.5

TABLE II.—Continued

Type (compound)	Retention Index									Pyr. temp. ° C.
	CO80	$CH_4$100	$CO_2$123	$C_2H_4$165	$C_2H_6$200	$NH_3$207	H_2O214	H_2S218	$C_3H_8$283	
Amine (F):										
$CH_3(CH_2)_6CH_2NH_2$		15		42	6	2	10	25		656.5
$CH_3(CH_2)_5CH_2NH_2$		14		46	9	2	7	23		656.0
$CH_3(CH_2)_4CH_2NH_2$		7		53	15	3	11	11		656.0
$CH_3(CH_2)CH_2NH_2$		21		51	6	3	9	11		656.5
Mercaptan (G):										
$CH_3(CH_2)_8CH_2SH$		13		29	12			14	30	657.0
$CH_3(CH_2)_5CH_2SH$		13		23	10			24	25	657.0
Ethanol amine (H): $NH_2CH_2CH_2CH$	8	3	1	10	1	5	8			

These particular compounds were pyrolyzed under the temperature conditions indicated in the far right column. The retention index for each of these dissociation products is listed at the head of each column. If desired, typical pyrogram or other retention time and peak area information for many different chemicals may be stored in computer storage for subsequent retrieval and automatic identification of the compound pyrolyzed. Alternatively such information may be accumulated and stored in tabular form for comparison and identification purposes if desired. In these cases the reference pyrograms or cracking patterns are obtained by individually pyrolyzing a variety of chemicals under controlled conditions. Each pyrolyzed chemical has its pyrolysis products passed through a chromatographic column for separation and detection. The detector output signal is recorded to obtain the control pyrogram for each chemical.

A preferred system for performing the method of this invention and thereby identifying small as well as large molecules is illustrated in FIG. 2. This simultaneous analysis of the large molecules provides much useful information as described in the said Levy application. By separating and detecting the large molecules contained in the pyrolysis products and noting their relative amounts, information relative to the carbon skeleton of the parent molecule may be obtained. Ratios of the quantities of the pyrolysis products to each other and to the total quantity of pyrolysis products, has been found to be uniquely indicative of the identity of the pyrolyzed sample components. This relationship is described in a paper entitled "Mechanism of Some Chain Reactions" by R. O. Rice and H. F. Herzfeld in the Journal of American Chemical Society, vol. 56, page 284, published in 1934.

In FIG. 2, a suitable source **10** of carrier gas is connected to a first gas chromatograph **32** having a non-destructive effluent detector **42**, such as a thermal conductivity detector. In the alternative, an effluent splitter and a destructive detector such as a flame detector of conventional type may be employed. The gas chromatograph **32** is conventional and typically includes an injection port **44**, a separating column **46**, and the detector **42**. The sample mixture may be injected through a sample inlet or septum **16** in the injection port of known type. The rate of flow through the chromatograph **32** may be regulated by a suitable flow controller (not shown). The output of the detector **42** is connected to the first port **48** of a two-way, four port switching valve **34**. The switching valve **34** is illustrated in its first, or sampling, position by the solid lines and its second, or non-sampling, position by the dotted lines. (The first and second positions of all two-way valves illustrated in the drawings are denoted by solid and dotted lines.) All conduits or gas flow connections illustrated in the drawings comprise any suitable tubing, such as stainless steel or other tubing as desired.

The second port **50** of the switching valve **34** is connected to a vent to atmosphere or other exhaust. The third port **52** of the valve **34** is connected to a flow controller **54** which regulates the carrier gas flow rate from the carrier gas source **10** via a conduit **19**. The sampling system **14** including a sample inlet **16**, if desired, may be included in the conduit **19** between the second flow controller **54** and the valve **34**. The fourth and final port **56** of the valve is connected through a conduit to a delay coil or loop **58** which may be nothing more than an unobstructed coil of stainless steel tubing having a desired volume. Such volume imparts a time delay to the components transit time through the system. The switching valve **34**, as well as the delay loop **58**, are enclosed within a sampling oven denoted by the dashed line enclosure **60**. The sampling oven **60** may be adjusted to maintain such temperature as is necessary to prevent condensation of the eluted sample component. The length and diameter of the delay loop **58** should be selected to provide sufficient volume for containing the entire amount of any given eluted sample component from the gas chromatograph **10** in vapor or gaseous form. The delay loop may be omitted if the sample is to be introduced directly through the sampling system **14**.

From the delay loop **58**, the second flow stream is directed by a suitable conduit through an open quartz, gold, or other non-reactive, high temperature pyrolysis tube **72** enclosed within a pyrolysis oven **74** and thence through one side of a pyrolyzate detector **76**. This pyrolyzate detector **76** preferably is a non-destructive detector such as a thermal conductivity detector having an analytical and reference side or cell. The detector **76** preferably is enclosed in a separate detector oven **80**, as is customary in gas chromatography, to facilitate precise control of the detector's temperature.

From the pyrolyzated detector **76**, the second flow stream, containing the now pyrolyzed sample components, is directed through an effluent splitter **78** which preferably provides a 1:1 split ratio. The two split flow streams are directed respectively to a second gas chromatograph, denoted by the dashed enclosure **24**, and if desired to a third chromatograph, shown in FIG. 2A to simultaneously detect large molecules as taught by Levy. The third chromatgraph **116** is substantially identical to the second, except for the backflush valve, contained in the second chromatograph, but its column is selected to separate larger molecules rather than small. Carrier gas for the third chromatograph **116** comprises the third separate flow stream or system and is derived from a flow controller **112** connected to the carrier gas source **10**. Returning now to the second chromatograph **24**, from the effluent splitter, the split second flow stream is connected to the first port **82** of a two-position, six-port switching valve **81** which selectively interconnects the gas streams directed to and from different adjacent pairs of its six ports **82**, **84**, **86**, **88**, **90** and **92** together. Although a rotary valve is illustrated diagrammatically, a linear motion valve or other known type may be employed if desired.

In the first position of the switching valve **81**, as illustrated by the solid lines, the second flow stream on entering the first port **82** passes out of the second port **84** to a sample loop **87**. This sample loop **87** may be, for example, an open or unobstructed stainless steel tubing wound in the form of a helix. The sample loop **87** must be of sufficient volume or capacity to contain at one time all of the pyrolysis products resulting from pyrolysis of the sample in their vapor or gaseous form. From the sample loop **87**, the second fluid stream passes back through the fifth port **90** of the six-port switching valve **81**, thence out of the sixth port **92** and out to vent or atmosphere.

In its second switching position, denoted by the dotted lines, the switching valve **81** interconnects those pairs of ports **84–86, 88–90, 82–92** necessary to introduce the sample contained in gaseous or vapor form in the sample loop **87** into a fourth separate flow system or stream.

Carrier gas for the fourth flow system is derived from a third flow controller **94** connected to receive carrier gas from the carrier gas supply **10**. Carrier gas forming the fourth flow system passes through a conduit **21** and a surge coil **96**, which along with the sample loop **87**, switching valve **81**, a backflush valve **159** a small molecule separating column **100** and a detector **76** form the second chromatograph **24**. The surge coil **96** aids in preheating the carrier gas in the fourth flow system. Its length and diameter or volume depend on the volume of the sample loop **87**, as will be described. From the surge coil **96**, the fourth flow stream continues by way of a suitable conduit, as described, through the fourth port **88** of the switching valve **81**, thence out of the third port **86** to the first port **160** of a two position four port backflush valve **159**, out through port **162** to the column **100**, and then in the third port **166**, out the fourth port **161** to the remaining side (reference) of the detector **76**. After desired low molecular weight components have been separated and detected and while the higher molecular weight components are still in column **100**, the backflush valve **159** is switched to the second or dotted line position. The same carrier gas flow will now backflush high molecular weight compounds from column **100** into detector **76** to clean out column **100** preparatory to making subsequent runs.

The second chromatograph **24** should have a carrier gas obtainable from a 50 to 100 pounds per square inch (p.s.i.) helium line, and desirably can be an isothermal, single column gas chromatograph using a non-specific detector such as a thermal conductivity detector. Suitable chromatographs for use in the first and fourth flow streams are available from Hewlett-Packard Company of Palo Alto, Calif., and are designated Model 5750. In each case the chromatograph detectors **42** and **76** and sampling systems **14** and **44** may be enclosed in separate ovens to insure accurate temperature control. The chromatograph detector **42** as well as the pyrolyzate detector **76** may be connected to suitable indicating devices as chart type potentiometric recorders. These provide a visual record of the amplitude variations of the respective detector output signals as a function of time.

In accordance with this invention, the separating column **100** is packed with suitable packing to permit or facilitate the separation of the small molecules present in the pyrolysis or dissociation products. The packing in this case may be the same as that employed or described in connection with separating column **24** in FIG. 1. The column of the third chromatograph **116** is packed to separate large molecules. One such packing may be "Diatoport S" liquid phase having a stationary phase of "Apiezon L," although "Triton X–305" may be preferred for the more polar molecules, both of which are available commercially.

The output of the detector **76** is connected to an indicator-timer denoted by block **104**. The indicator as described may be a recorder. The timer may be a conventional clock mechanism which is actuated by a mechanical linkage denoted by the dash-dot line **106**. This linkage **106** is the same as that which is employed to actuate the valve **81** from a suitable knob **108**. Thus when the valve **81** is switched to introduce the dissociation products contained in the sample loop **87** into the separating column **100**, the timer is switched on. With the occurrence of each peak, a microswitch on the recorder, sensing the recorder pen displacement, may cause the timer to print out the time, or store the time in a register for later digital handling of the information. In the alternative, the time may be measured manually by the operator directly from the chart record. These retention times may then be related as previously described to the functional groups, and therefore are helpful in establishing the identity of the parent molecules present in the original sample.

In one embodiment of the invention that was constructed, the delay loop **58** was constructed of 3/16" stainless steel tubing having a length to provide a delay volume of 50 milliliters. The sample loop was of similar dimension. All connecting conduit or tubing employed was 1/8" stainless steel and the flow rate in the second stream **19** through the pyrolysis tube **72** was adjusted by flow controller **54** to be 6 cc. per minute. The quartz pyrolysis tube was 45 centimeters in length and 3/16" in diameter. The surge coil **96** was 15' of 3/16" stainless steel tubing. The flow rate of the first flow stream was adjusted to be approximately 20 cc. per minute and a 1/8" analytical column **46** packed with "Apiezon L" on "Diatoport S" was employed. The separating column **100** was similarly packed.

The third chromatograph **116** is shown in FIG. 2*a*. Carrier gas for the third chromatograph is derived from the second flow controller **112**. This carrier gas, which comprises a third flow system, passes through the conduit **23**, through the flow controller **112**, thence through the conduit **114**, surge coil **118**, a six port, two way valve **140**, a large molecule separating column **156** and a detector **158** to vent. These elements together with a sample loop **154** make up the third chromatograph **116**. All of the elements are substantially identical in location and function to the elements of the second flow system and hence need not be described further. The surge coil **118** aids in preheating the carrier gas in the third flow system as was the case in FIG. 2. The output of the detector **158** is connected to an indicator-timer **160** which is actuated through the linkage **162** denoted by the dotted line by the knob **164**. This is the same knob which turns the switching valve **140** as was the case in FIG. 2.

The pyrolyzate from the splitter **78** through the first port **142** of the valve **140**, out of the second port **144**, through the sample loop **154** in a reverse direction, thence back through the fifth port **150** and out of the sixth port **152** to vent. Since the system described is substantially identical to that of the second chromatograph **24**, no further description is deemed necessary. The only difference between the two systems is the fact that the separating column **156** is suitably packed to separatel arge molecules rather than small. This eliminates the necessity of utilizing the backflush valve **150** as is preferred in the small molecule separation using the system of FIG. 2.

With the use of the second and third chromatographs, the large as well as the small molecules appearing in the pyrolysis products may be simultaneously separated and their respective elution times measured and recorded. From this data a wealth of information as to the identity of the parent molecule is obtainable. If desired a single indicator-timer **160** may be used. In this instance the single knob **108** (FIG. 2) actuates both valves **140** (FIG. 2*a*) and **81** (FIG. 2).

In a typical analysis made in accordance with the method of this invention the first switching valve **34** (FIG. 2) is placed in its second position such that the eluent from analytical column **46** is passed to vent. Suitable flow rates for the second and fourth flow streams **19** and **21** are established as previously described, i.e., high for chromatographic separation and low for pyrolysis. The temperature of the several detector ovens **60**, **74** and **80**, as well as the several chromatograph ovens, not separately shown, are brought up to their desired optimum operating temperatures. Assume that a one microliter sample is injected into the injection port **16** of the first flow system by a microliter syringe.

When the first chromatograph detector **42** indicates, by an increase in amplitude of the detector output signal, that the desired sample component, whose identity is to be determined, is being eluted, the first switching valve

34 is switched either manually or automatically from the second position, as illustrated by the dotted lines, to the first position as illustrated by the solid lines. The carrier gas plus separated sample component eluted from the first flow stream are passed into the delay loop **58** and the carrier gas forming the second flow stream (conduit **19**) is vented. Just before the sample component to be identified is completely eluted, as denoted by the amplitude of the detector **42** output signal returning to its reference or zero level, or a corresponding peak on a recorder tracing returning to baseline, the first switching valve **34** is returned to its second position. The regulated flow of the second flow stream, isolated from that of the first flow stream, directs the flow of the sample component stored in the delay loop **58** thru the pyrolysis tube **72**.

As flow through the pyrolysis tube **72** continues, the sample component is pyrolyzed and the pyrolyzate or dissociation or thermal decomposition products pass through the pyrolyzate detector **76**, splitter **78**, switching valve **81**, sample loop **87** and vent. Variations in the amplitude of the pyrolyzate detector **76** output signal as a function of time are observed. Once the first output signal from detector **76** returns to its quiescent value or baseline, as is described more fully in the said Levy application, the six-port switching valve **81** is switched from its first to its second position, as illustrated by the dotted lines. The pyrolyzate has by now passed into the sample loop **87** flowing in one direction.

Upon switching the valve **81**, carrier gas in the fourth flow stream (conduit **21**), passing through the surge coil **96**, flows through the sample loop **87** in the opposite direction and backflushes the pyrolyzate from the sample loop **87**. Such backflushing generally compresses the pyrolyzate and returns it to a more compact, slug-type sample for passage through the backflush valve **98** and the analytical column **100** of the fourth flow stream (conduit **21**). The surge coil **96** aids in the compression and integration of the pyrolyzate into the third flow stream. This third stream generally has a higher flow rate than the second flow stream and may be of different temperature and pressure. The surge coil **96**, preferably having a volume exceeding that of the sample loop, reduces the effect of these disturbances. The extra volume provided by the surge coil **96** serves to damp out transitory flow rate fluctuations, which affect detector accuracy.

The flow through the pyrolysis tube **72** is relatively slow to insure good heat transfer to the compounds and at a low pressure so as to inhibit secondary reactions during pyrolysis. On the other hand, the flow rate in the fourth flow stream is at a relatively high flow rate. When the extra pressure of the third flow stream is applied through the sample loop **87** for the backflush operation, the surge coil **96** acts as a reservoir so as to more quickly, and with less flow disturbance, adjust the flow rate in the sample loop **87** to that desired. The dissociation products now are separated by the separating column **100** and detected by the reference side of the pyrolyzate detector **76**. Backflushing of the separating column **100** may be performed as described. The operation of the third chromatograph of FIG. 2*a* is substantially the same and need not be separately described.

If desired, the separating column **100** may be packed with a packing capable of separating not only the small molecule decomposition products, but also the large molecules as well. In this single column operation either a single non-specific detector can be employed, or multiple detectors, one of which must be sensitive to the small molecules such as thermal conductivity detector and the second, which preferably should be a flame detector. The multiple detectors can either be in the series or in parallel. This permits the simultaneous use of small molecules for identification of the functional groups of the parent molecule, as well as the use of the larger molecules for the determination of the carbon skeleton of the parent molecule in accordance with the Rice-Herzfeld theory. In this event the effluent splitter **78** and third chromatograph **116** may be omitted.

An alternative embodiment to the system and method just described is that illustrated in FIG. 3 in which the splitter **78** and third chromatograph **116** are eliminated and the effluent from the surge coil **96** (FIG. 2), after passing through the six-port valve **81**, and out the third port **86**, is passed on to an effluent splitter **150** similar to effluent splitter **78**. In this case, however, the split ratio may be 10:1 with 10 parts going through a small molecule separating column and the 1 part going through the large separating column. The large molecule separating column **154** may be packed as hereinbefore described. The small molecule separating column **152** may be packed with the "Polypak" material described hereinbefore. Silicon oil on a "Teflon" packing may be equally advantageously employed for the small molecule columns.

Separate programming ovens may be used for columns **152** and **154** respectively. The output of the small molecule column **152** is connected through a suitable nondestructive detector such as thermal conductivity (TC) detector **156**, whereas the output from the large molecule separating column **154** is preferably connected through a flame ionization detector **158**. The output of each detector **156** and **158** is passed to vent. The electrical output of the TC detector **156** is coupled to a suitable indicator and timer **104** (FIG. 2). The flame ionization detector electrical output may also be connected to an indicator such as a chart recorder. In this manner, the separation and analysis of the small as well as the large molecules contained in decomposition products, is obtained simultaneously.

Still another alternative embodiment of the invention for obtaining a simultaneous analysis of both the small and large molecules pyrolysis products is illustrated in FIG. 4. In this embodiment, the pyrolyzate is passed from the surge coil **96** (FIG. 2) through the third valve port **86** (FIG. 2) to a second six-port, two position valve **180** (FIG. 4) which may be substantially identical in construction to the switching valve **81**. The second port **174** of the valve **170** is coupled through a suitable conduit to the small molecule separating column **152** and thence to the fifth-port **180**, out the sixth port **182** to a TC detector **156** and thence to vent. The second position of the valve **170** is denoted by the dotted lines. Gas from the source **10** passes through the fourth port **178**, out the third port and through the large molecule separating column **154** and detector **158** to vent.

The pyrolyzate from the sample loop **87** enters the small molecuule separating column **152**, is separated into its respective components and detected by the detector **156**. When the several small molecule products have been detected, and before the large molecules are given an opportunity to pass through the small molecule column **152**, the switching valve **170** is switched to its second position. In this position, flow is from the carrier gas source **10** into the fourth port **178**, out the fifth port **180**, and back through the small molecule column **152** in a reverse direction so as to backflush the column. This compresses the remaining large molecules into a compact slug and carries them into the second port **174**, out of the third port **176** and through the large molecule column **154** which separates the large molecules of the pyrolyzate. These separated large molecules are detected by the detector **158** in the same manner as described.

It will be obvious that various modifications may be made in the apparatus and in the manner of operating it. It is intended to cover such modifications and changes as would occur to those skilled in the art, as far as the following claims permit and as far as consistent with the state of the prior art.

What is claimed is:

1. A method for analyzing an unknown organic material compound while having on hand for reference a

multitude of separate control cracking patterns obtained by individually pyrolyzing a variety of chemicals under controlled conditions and in each instance passing the pyrolysis products produced from a given chemical to a chromatographic column and obtaining control cracking patterns thereby for said given chemical, said method comprising the steps of:

passing a sample of the unknown to be analyzed to a pyrolyzing chamber,

pyrolyzing the sample under substantially the same conditions as were used in obtaining said control cracking patterns to obtain pyrolysis products,

passing the pyrolysis products through a splitter for dividing the pyrolysis products in to two portions by volume, simultaneously separating the most volatile, low molecular weight pyrolysis products contained in one of said portions and the less volatile, high molecular weight pyrolysis products contained in the other of said portions in first and second chromatographic columns respectively, and obtaining thereby first and second partial cracking patterns for said sample, and

comparing said partial cracking patterns to said control cracking patterns for identification purposes, thereby determining the kind of said sample.

2. A method according to claim **1** which includes the additional step of detecting the effluents of said first and second chromatographic columns, thereby to obtain said partial cracking patterns.

3. A method according to claim **1** wherein before the first passing step there are included the additional steps of:

passing said sample through a chromatographic separating column, thereby successively eluting components of said sample, and

selecting predetermined ones of said eluted components to be passed through said pyrolyzing chamber.

4. Apparatus for analyzing an unknown organic material compound while having on hand for reference a multitude of separate control cracking patterns obtained by individually pyrolyzing a variety of chemicals under controlled conditions and in each instance passing the pyrolysis products produced from a given chemical to a chromatographic column and obtaining a control cracking pattern thereby for said given chemical, said apparatus comprising:

a pyrolysis chamber,

means for passing a sample of the unknown to be analyzed through said pyrolysis chamber, under said controlled conditions, thereby to obtain pyrolysis products of said sample,

splitting means having an input connected to the output of said pyrolysis chamber and first and second outputs for dividing the pyrolysis products into two portions by volume,

first and second chromatographic separating columns connected to simultaneously receive the pyrolysis products from said first and second outputs of said splitting means, respectively;

said first chromatographic column being capable of separating the most volatile, low molecular weight pyrolysis products of said sample to provide a first partial cracking pattern;

said second chromatographic column being capable of separating the less volatile, high molecular weight pyrolysis products of said sample to provide a second partial cracking pattern;

wherein said first and second partial cracking patterns for said pyrolysis products can be related to said control patterns for determining the kind of sample.

5. The apparatus according to claim **4** which also includes detector means coupled to the output of each of said first and second chromatograph columns for providing said cracking patterns.

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U.S. Cl. X.R.

23—230, 253, 254; 55—67; 73—23.1

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,518,059 Dated June 30, 1970

Inventor(s) Eugene J. Levy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, Table II, under the heading "Pyr. temp. °C." the fifth item "656.0" should read -- 656.5 --;

Column 7, Table II, under the group heading "Amine (F)" the last-named formula "$CH_3(CH_2)CH_2NH_2$" should read -- $CH_3(CH_2)_3CH_2NH_2$ --;

Column 10, line 37, after "78" insert -- passes --; line 46, "separatel arge" should read -- separate large --.

SIGNED AND
SEALED
SEP 29 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

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